

## 2E Analysis of a Renewable Hydrogen Plant Based on the Bio-Steam Reforming (BSR) System

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**ABSTRACT:** *In this paper, a biogas water vapor reforming system for hydrogen production is presented. The biogas mixture contains a large percentage of methane and carbon dioxide and small amounts of other gases. Thermodynamic modeling (energy and exergy) is performed on the proposed system and a study on the effect of various system parameters such as temperature and molar ratio of carbon dioxide to methane in the biogas mixture on hydrogen production, energy, and exergy efficiency of the whole system has been done in this paper. The results show that the increase in steam reforming reactors in a constant molar ratio of carbon dioxide to methane in the biogas mixture increases hydrogen production and the energy and exergy efficiency of the system. However, increasing the molar ratio of carbon dioxide to methane in the biogas mixture at high temperatures reduces hydrogen production per mole of methane, and as a result, the energy and exergy efficiency of the whole system is reduced. Also, the highest energy and exergy efficiency of the whole system in the conditions where the amount of hydrogen production is maximum is 52% and 42%, respectively.*

**KEYWORDS:** *Steam Methane Reforming (SMR); Biogas; Hydrogen production; Energy analysis; Exergy analysis; Bio-Steam Reforming (BSR).*

### INTRODUCTION

Hydrogen is recommended as a clean energy carrier used for environmentally friendly energy production, mainly used in power plants and chemical industries [1,2]. In addition, it can be effectively converted to electricity in fuel cell systems with minimal greenhouse effects. [3,4]. Today, hydrogen can be produced through fossil fuel sources, hydrocarbon reforming processes, and water

electrolysis [5]. For this purpose, biogas, as one of the most widely used renewable energy sources, can be used instead of fossil fuel sources to produce power and hydrogen, which plays an important role in minimizing global warming [5,6]. Biogas can be obtained by the anaerobic fermentation and decomposition of biomass from various organic materials, containing 1 to 3% by volume of

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methane and 30 to 40% by volume of carbon dioxide. However, a greater methane ratio means a higher hydrogen production rate and because of that biogas containing more methane concentration is more suitable and can be effectively converted to hydrogen by various reforming processes (Also, there are some new technologies such as carbon dioxide utilization of carbon dioxide hydration can transform  $\text{CO}_2$  to methane) [6,8]. Results showed that a typical SMR process has a higher hydrogen production ratio among the currently available types of reforming processes, such as partial oxidation, autothermal reforming, and steam reforming [9].

Simultaneous energy and exergy analysis in biogas water vapor reforming systems can be a good idea to increase performance and hydrogen production in this type of system [10]. According to the first law of thermodynamics, system energy analysis calculates the amount of energy required in the form of work and heat to start the process and can not determine whether the reaction is feasible or impracticable. System exergy analysis is a useful tool that can quality examine the available energy and determine the irreversibility factors of the system such as chemical reactions, mixing, and heat transfer due to limited temperature difference and also by exergy analysis, exergy degradation of different system performance is identified and by providing suitable thermodynamic conditions. This method is usually used to enhance the exergy efficiency or energy usefulness which makes the most use of energy resources and as a result can improve the performance of the system [11].

In recent years, significant research has been done on hydrogen production from various biogas reforming processes [5-16]. *Changalex and Li* [12] investigated the biogas reforming process to produce hydrogen in a honeycomb-type reactor. The results showed that with increasing temperatures, the percentage of methane conversion and hydrogen production increases. *Kapiti et al.* [13] designed the effect of temperature and the molar ratio of water vapor to carbon between (1-5) by designing a biogas water vapor reforming reactor in the temperature range of 700-900 °C, both experimentally and theoretically. They concluded that with increasing temperature and the molar ratio of water vapor to carbon, the amount of hydrogen production increased, and at a temperature of 900 °C and the molar ratio of water vapor to carbon equal to 3, the molar fraction of hydrogen is 0.45. *Hajjaji et al.* [14] In a study,

by proposing a biogas reforming system, the environmental effect of hydrogen production as well as the effect of various parameters such as temperature and molar ratio of water vapor on carbon on the energy efficiency of the whole system and the amount of hydrogen production. Their results showed that the optimal conditions in which the total energy efficiency of the whole system (0.73) and the amount of hydrogen production is maximum, at a temperature of 800 °C, and the molar ratio of water vapor to carbon is equal to 3. *Ahmed et al.* [15] also parametrized the effect of temperature (590-690°C), the molar ratio of water vapor to carbon (1.28-3.86), and the molar ratio of carbon dioxide to methane (0.5-1.5) in the biogas vapor reforming process on the amount of hydrogen production and The other equilibrium, compounds performed the conversion percentages of methane and carbon dioxide conversion. The results showed that with increasing temperature, the maximum conversion percentages of methane and carbon dioxide at 685°C ( $S = 1.32$  and the molar ratio of carbon dioxide to methane of 0.98) was 94% and 1.9%. Also, changing the molar ratio of carbon dioxide to methane has little effect on hydrogen production.

In another study, *Zhou et al.* [16] evaluated changes in the molar ratio of carbon dioxide to methane in a biogas mixture on hydrogen production, system energy efficiency, methane conversion percentage, and carbon dioxide. More carbon dioxide and reduced methane conversion rates result in lower hydrogen production and little change in the system's overall energy efficiency. *Quadro et al.* [17] investigated hydrogen production through steam reforming processes and partial oxidation in conventional and microreactor systems. Hydrogen is more abundant in the water vapor reforming process. In a study, *Zinc et al.* [18] investigated the effect of temperature (923- 1173K), and the molar ratio of water vapor to carbon (1-2), on the biogas vapor reforming reaction. They concluded that at 1023K, the pressure of 1 bar and the molar ratio of water vapor to carbon is 1.5, and the optimal conditions for maximum hydrogen production are obtained. *Koeh et al.* [19] presented biomass reforming for hydrogen production by presenting a system, energy analysis, and exergy and showed that the whole system's maximum energy and exergy efficiencies are 22% and 19%, respectively. In a study by *Niko Khoahinat and Amine* [20], they studied the thermodynamic analysis of the methane carbon dioxide

reforming process in solid carbon formation and concluded that at high temperatures of 1073K, carbon formation decreases and hydrogen production increases. *Aydinoglu* [21] evaluated the combination of two carbon dioxide reforming processes and methane water vapor reforming. The results showed that the simultaneous reaction of these two reforming processes increases hydrogen production and reduces solid carbon formation. *China et al.* [22] investigated the thermodynamic analysis of the methane carbon dioxide reforming process at high pressures and concluded that increasing the pressure in the reforming reactions, the percentage of methane conversion and thus the amount of hydrogen production decreases. *Norouzi et al.* [23] also presented a system to perform exergy analysis of methane vapor reforming to produce hydrogen and evaluate the effect of different parameters on hydrogen production, energy efficiency, exergy efficiency, and exergy degradation of the components system. As the temperature rises to 904 K, more exergy degradation is achieved in the reformer. *Mehr et al.* [24] evaluated thermodynamic analysis and economic (economic) exergy, biogas reforming as feed for solid fuel cells, emphasizing anode and cathode recirculation. *Hiblot et al.* [25], in an experimental study, methane water vapor reforming of biomass gasification process in the high-temperature range between (1200-1800K) and concluded that at temperatures above K1700, methane is completely reformed and is converted to hydrogen.

In another study, *Grobman et al.* [26] evaluated the methane vapor reforming process at low molar ratios of water vapor to carbon between 0.1-0.4, 450-500C temperature and atmospheric pressure, and their results showed that for lower molar ratios of water vapor to carbon a lower external heat and power are required, and also with increasing temperature in low molar ratios, carbon formation is reduced which has a positive effect on hydrogen production. *Jang et al.* [27] studied the effect of combining water vapor and carbon dioxide reforming processes on different molar ratios of carbon dioxide and water vapor to methane and the molar ratio of carbon dioxide to carbon vapor in the temperature range between (500 and 1000 °C) They concluded that at a temperature of at least 850 °C and the molar ratio of water vapor and carbon to methane more than 1.2 and the molar ratio of carbon dioxide to steam (1: 1.2), there are suitable conditions

for the production of synthetic gas and also no carbon formation. In another study, *Anzelmo et al.* [28] investigated the process of natural gas vapor reforming to produce hydrogen in a Pd membrane reactor in the temperature and low-pressure range, and their results showed that the best performance of this reactor at 400C and 300kPa pressure for which the reaction rate is 84% methane conversion and 82% hydrogen production. *Tsai et al.* [29] also investigated the internal reforming of methane vapor in a solid oxide fuel cell using anode vapor recovery. They concluded that at temperatures above 750C and a molar ratio of oxygen to carbon above 1.2, more converted from 90% methane. A study by *Mahmoudan et al.* [30] investigated a novel integrated energy system based on a geothermal heat source and a liquefied natural gas heat sink proposed in this study for providing heating, cooling, electricity power, and drinking water simultaneously. As their results show the most excellent trade-off solution specified by the TOPSIS method, the system attains 29.15% exergy efficiency and 1.512 \$/GJ total product cost per exergy unit. The main output products are consequently calculated to be 101.07 kg/s cooling water, 570.44 kW net output power, and 81.57 kg/s potable water. *Hoseinzadeh and Heyns* [31] studied energy, exergy, and environmental (3E) analysis of a 400 MW thermal power plant. First, the components of the power plant are examined in terms of energy consumption, and subsequently, the energy losses, exergy destruction, and exergetic efficiency are obtained. In their model, it is observed that the exergetic efficiency and exergy destruction in the boiler are primarily affected by changes in the environmental temperature. Furthermore, by increasing the main pressure in the turbine, the load on the power plant is increased, and increasing the condenser pressure reduces the load on the power plant. In environmental analysis, the production of pollutants such as SO<sub>2</sub> production and CO<sub>2</sub> emission has been investigated. In a study by *Kariman et al.* [32], a high-performance Multi-Effect Desalination (MED) system is introduced and the enhancement potential of that is evaluated in detail. The introduced and reference designs are compared together from different points of view. The results showed that not only the freshwater production of the introduced MED device is enhanced from the range of 12–16 to 14–21.6 L/h compared to the base case condition, but also gained output ratio increases up to 30%–40%.

Hosseinzadeh *et al.* [33] studied the integrated carbon dioxide power cycle with the geothermal energy source to supply the required reverse osmosis desalination power for freshwater production. The optimal inlet discharge rate of the sodium hypochlorite generator was 62% of the brine water outlet discharge rate of the desalination system. Plus, the total cost rate is reduced by 10% compared to the general case when 100% of the brine water discharge rate of the desalination system enters into the sodium hypochlorite generator. The second case is multiobjective optimization to reduce costs and increase productivity. In the paper by *Tjahjono et al.* [34], a new configuration cycle is proposed using LNG as a heat source and heat sink. This new proposed cycle includes the CO<sub>2</sub> cycle, the organic Rankine cycle (ORC), a heater, a cooler, a NaClO plant, and reverse osmosis. This cycle generates electrical power, heating, and cooling energy, Potable Water (PW), hydrogen, and salt all at the same time. The results for each subsystem are validated by previous research in this field. This system produces 10.53 GWh of electrical energy, 276.4 GWh of cooling energy, 1783 GWh of heating energy, 17,280 m<sup>3</sup> potable water, 739.56 tons of hydrogen, and 383.78 tons of salt in a year. The proposed system's energy efficiency is 54.3%, while the exergy efficiency is equal to 13.1%. The economic evaluation showed that the payback period, the simple payback period, the net present value, and the internal rate of return is equal to 7.9 years, 6.9 years, 908.9 million USD, and 0.138, respectively. In this paper by *Ahmadi et al.* [35], solar energy technologies are reviewed to find out the best option for electricity generation. Using solar energy to generate electricity can be done either directly or indirectly. In the direct method, PV modules are utilized to convert solar irradiation into electricity. In the indirect method, thermal energy is harnessed by employing Concentrated Solar Power (CSP) plants such as Linear Fresnel collectors and parabolic trough collectors. In this paper, solar thermal technologies including solar trough collectors, linear Fresnel collectors, central tower systems, and solar parabolic dishes are comprehensively reviewed and barriers and opportunities are discussed. In addition, a comparison is made between solar thermal power plants and PV power generation plants. Based on published studies, PV-based systems are more suitable for small-scale power generation. They are also capable of generating more electricity in a specific area in comparison with CSP-based systems. However,

based on economic considerations, CSP plants are better in economic return. In their paper, *Ahmadi et al.* [36] analyzed energy and exergy thermodynamics, as well as the exergy-economic analysis of the Proton Exchange Membrane (PEM-type) electrolysis process for hydrogen production, which derives its driving power from ground-based power. For this purpose, the required work is generated from the geothermal source by the Rankine cycle. The resulting work is used as an input for the electrolysis process and electrolysis water is preheated by geothermal sewage treatment. Functional parameters based on the first and second thermodynamic rules are determined for the system and the performance of the system has been evaluated. The effects of geothermal water temperature and electrolysis on the amount of generated hydrogen have been studied and it has been shown that these parameters correlate with each other. Also, energy, exergy, and thermo-economic analysis methods have been carried out using MATLAB software. Also in another paper by *Ghazvini et al.* [37], initially a concise summary of present and advancing hydrogen production technologies is presented, and secondarily a comprehensive review of research associated with hydrogen production based on geothermal energy is provided. Thirdly, the process descriptions of geothermal-assisted hydrogen production coupled with its technical, economic, and environmental aspects are addressed. Finally, comparative assessments of costs and environmental aspects related to hydrogen production based on different energy sources have been performed. By the results, the geothermal-assisted hydrogen production cost based on electrolysis is competitively lower than other sources like wind, and solar thermal coupled with natural gas, solar PV, and grid. Also, the same behavior can be seen for geothermal-assisted hydrogen production costs based on the thermochemical process.

In general, in the literature, only a few researchers have studied the effect of different thermodynamic parameters in biogas steam reforming on the amount of hydrogen production, energy efficiency, and exergy systems [37-40]. An energy and exergy analysis using the proposed system for the solar biogas water vapor reforming process to produce hydrogen has been investigated in this research. The main objectives of this research are:

- Introducing a system for hydrogen production from the biogas water vapor reforming process using solar energy

- A thermodynamic modeling and Exergy analysis of the proposed system
- Parametric study to investigate the effect of various parameters such as temperature and molar ratio of carbon dioxide to methane in biogas mixture on system performance

## THEORETICAL SECTION

### Case description

Fig. 1 shows the schematic of the solar biogas water vapor reforming system considered in this research. The purpose of this system is to produce hydrogen from biogas water vapor reforming. In this form, a mixture of biogas (flow 1) enters the system on one side and water vapor (flow 3) on the other side through pumps and mass flow controllers to control the molar ratio of water vapor to carbon and carbon dioxide to methane and total flow rate. They enter the process. The biogas in the storage tank (flow 1) is preheated by the flow of steam-reforming exhaust gases (flow 9) in the heat exchanger, and on the other hand, the water vapor (flow 3) is preheated using the same heat flow as the gases (flow 10). And then in the evaporator, the vapor becomes saturated steam. The preheated currents and the saturated vapor flow (5, 2) are mixed in the mixer and reheated in the reactor using the high temperature of the reforming reaction products (flow 8) to prepare the conditions for the chemical reforming reaction in the reactor. . Also, due to the biogas water vapor reforming reaction at high temperature, a solar source is used to provide the reaction heat [41], which will be modeled on the reactions performed in the reactor in the following sections. Fig. 1 converts solar energy into chemical energy in a reactor in the following description of the system. Then the flow of reaction exhaust gases in the reactor, which includes the chemical compounds of hydrogen, carbon monoxide, carbon dioxide, methane, and water vapor, as stated to make optimal use of the high heat of this flow (8) to preheat the mixture of biogas and biogas steam. The flow of cooled gases, which has a higher molar fraction of hydrogen than other compounds (11) to produce the hydrogen needed also loses some of its heat in the radiator. Finally, by purification processes, hydrogen (flow 13) can be separated from synthesis gas and used as feed to generate electricity from fuel cells and other systems [42].

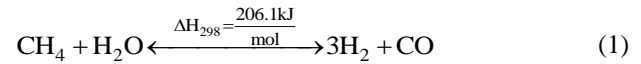
### Methodology

In this paper, EES software is used as the main tool in all calculations.

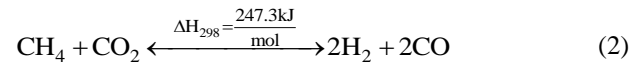
### Chemical reactions performed by the reactor

The biogas water vapor reforming process performed in the reactor can be a general combination of the following equilibrium reactions [43-45].

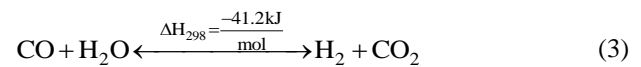
Methane vapor reforming reaction (SMR):



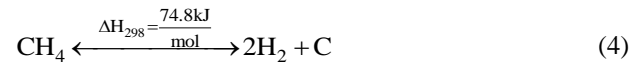
Reforming reaction of methane carbon dioxide (CMR):



Water Gas Shift (WGS) Reaction:



Methane Decomposition Reaction:



Both reactions (SMR) and (CMR) are highly endothermic, so a suitable heat source must perform the reaction. In this paper, the reaction heat is provided by a solar source [1]. The Water-Gas Shift (WGS) reaction is also exothermic and is suitable at low temperatures (500-600K) [34]. The main limitation of the CMR reaction is the possibility of carbon formation (in the methane decomposition reaction), and the need for a temperature source is high to react [17]. Therefore, to increase the amount of hydrogen production and reduce the formation of carbon, it is necessary to optimize the molar ratio of water vapor to carbon and the reaction temperature [6,45].

### Gibbs free energy minimization

Gibbs free energy minimization is commonly used in systems in which chemical reactions occur to obtain the molar fraction of chemical compounds in equilibrium mode [46] because in the chemical equilibrium state, the total free energy of Gibbs is minimized. The total free energy of Gibbs of a system at a certain temperature and pressure is expressed as follows [47]:

$$G = \sum_{i=1}^{NC} n_i \mu_i \quad (5)$$

that  $n_i$  is the number of equilibrium moles, and  $\mu_i$  is the chemical potential for component  $i$ , which is defined as follows:

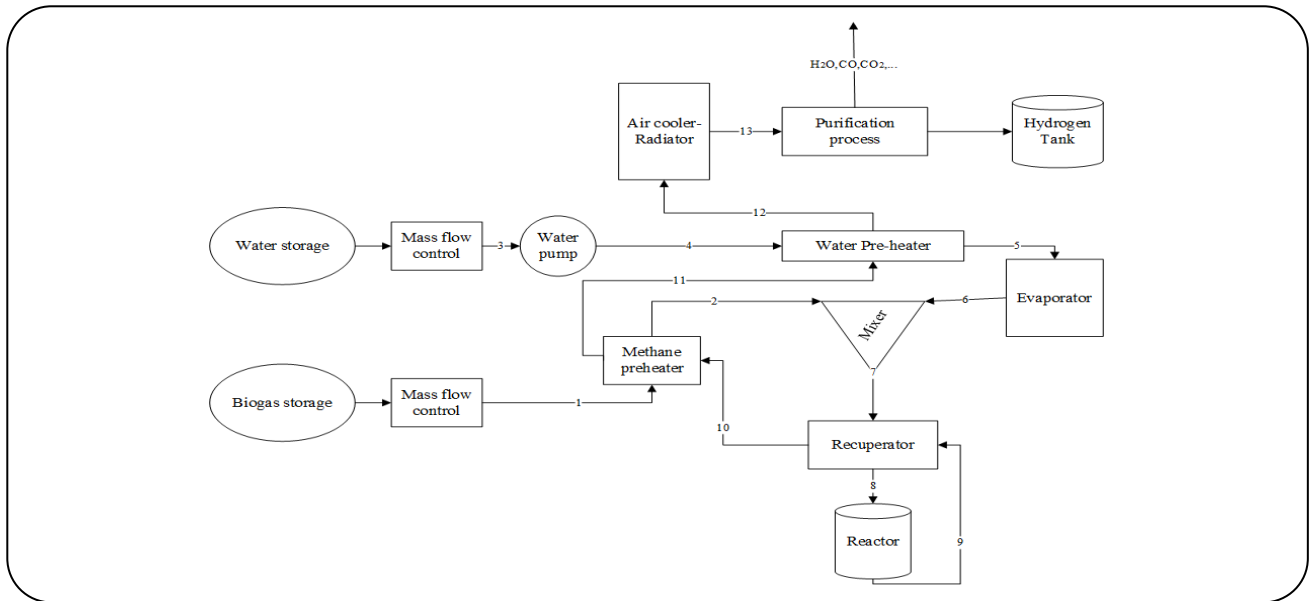


Fig. 1: Solar biogas steam reforming system.

$$\mu_i = \mu_i^o + R_{\text{univ}} T \ln \left( \frac{f_i}{f_i^o} \right) \quad (6)$$

$\mu_i^o$  is the chemical potential of component  $i$  at temperature  $T$  and standard pressure, which is equal to the Gibbs molar free energy, is expressed as follows (symbol 0 indicates the standard state):

$$\mu_i^o = \bar{g}_i^o = \bar{h}_i^o - T \bar{s}_i^o \quad (7)$$

$f_i^o$  is the fugacity of component  $i$  in the reference state in the gaseous and  $P^o$  (standard gas pressure), and  $f_i$  is the fugacity of component  $i$  in the mixture in the gaseous state is obtained from the following equation:

$$f_i = \varphi_i \cdot y_i \cdot P \quad (8)$$

$y_i$  is the molar fraction of component  $i$  in equilibrium, and  $\varphi_i$  is the fugacity coefficient.

Component  $i$ , the value of which is approximately at high temperatures and low pressures. Assuming  $\varphi_i = 1$  and placing Equations (6-8) in Equation (5), the total free energy of Gibbs is as follows:

$$G = \sum_{i=1}^{NC} n_i \left( \mu_i^o + R_{\text{univ}} T \ln \left( \frac{y_i P}{P^o} \right) \right) \quad (9)$$

If in the chemical equilibrium state a solid phase such as carbon is also in the reaction products because the solids

do not have vapor pressure, determining the chemical potential of these materials (carbon) is done as follows[48, 49]:

$$\mu_c = \mu_c^o = \bar{g}_c^o = \bar{h}_c^o - T \bar{s}_c^o \quad (10)$$

By equating Equations (10) to (9), the total free energy of Gibbs with a solid carbon phase is as follows:

$$G = \sum_{i=1}^{NC} n_i \left( \mu_i^o + R_{\text{univ}} T \ln \left( \frac{y_i P}{P^o} \right) \right) + N_c \mu_c^o \quad (11)$$

Where  $n_c$  is the number of moles of carbon in equilibrium and  $\mu_c^o$  is the chemical potential of carbon in the standard state. The Lagrange coefficient method has been used in this paper to obtain chemical compounds in equilibrium using Gibbs energy minimization. The advantage of this method is that there is no need to know equilibrium reactions; it is enough to know the composition of materials in equilibrium, it has good convergence power and there is no limit to a large number of equilibrium reactions, and it is also used for temperatures below 700 K [37]. Also, because in equilibrium, Gibbs free energy reaches its lowest value, in general, using the Lagrange method, the minimum Gibbs free energy in equilibrium is expressed as follows [50]:

$$0 = \sum_{i=1}^{NC} n_i \left( \mu_i^o + R_{\text{univ}} T \ln \left( \frac{y_i P}{P^o} \right) + \sum_k \lambda_k a_{ik} \right) + N_c \mu_c^o \quad (12)$$

Which  $\lambda_k$  is the Lagrangian coefficient. In minimizing Gibbs free energy, the following limitations must be met, the molar value of the material must be positive:

$$n_i \geq 0 \quad i = 1, \dots, NC \quad (13)$$

$NC$  is the number of equilibrium components. The number of atoms in each chemical component remains constant in equilibrium according to mass survival according to the following equation:

$$\sum_i n_i a_{ik} = A_k \quad k = 1, \dots, NE \quad (14)$$

$NE$  is the number of elements (atoms) in equilibrium.

### Energy and exergy analysis

Equations (17) have been used to determine hydrogen production per mole of methane [17]. The molar ratio of steam to carbon at the beginning of the reaction:

$$S_c \text{ (ratio)} = \left( \frac{n_{H_2O}}{n_{CH_4}} \right)_{in} \quad (15)$$

The molar ratio of carbon dioxide to methane in biogas mixture:

$$\frac{CO_2}{CH_4} = \left( \frac{n_{CO_2}}{n_{CH_4}} \right)_{in} \quad (16)$$

Hydrogen production per mole of methane:

$$y_{H_2} = \frac{(n_{H_2})_{out}}{(n_{CH_4})_{in}} \quad (17)$$

$(n_{CO_2})_{out}$  is the mole of hydrogen leaving the reforming reaction and  $(n_{CH_4})_{in}$  is the mole of methane entering the biogas mixture.

Assuming stable conditions for each control volume shown in Fig. 1, the mass and energy balance for each component of the system will be as follows [11]:

Mass balance:

$$\sum \dot{m}_i = \sum \dot{m}_o \quad (18)$$

Energy balance:

$$\sum \dot{E}_{in} = \sum \dot{E}_{out} \quad (19)$$

Where  $\dot{E}_{in}$  is the amount of input energy and  $\dot{E}_{out}$  is the amount of output energy to the control volume.

General system:

The energy efficiency of the general system for hydrogen production is expressed as follows [39]:

$$\eta_{en,tot} = \frac{\dot{n}_{H_2} \overline{LHV}_{H_2}}{\dot{n}_{biogas} \overline{LHV}_{Biogas} + \dot{Q}_{reactor} + \dot{Q}_{vap} + \dot{W}_{pump}} \quad (20)$$

$\dot{n}_{H_2}$  is the molar flow rate of hydrogen produced (current 13),  $\overline{LHV}_{H_2}$  is the Low calorific value of hydrogen [5],  $\dot{n}_{biogas}$  is the primary flow rate of biogas mixture Flow 1 (mixture of carbon dioxide and methane),  $\overline{LHV}_{biogas}$  is the Low calorific value,  $\dot{Q}_{reactor}$  is the heat required for the reaction in the reactor,  $\dot{Q}_{vap}$  is the amount of heat required to evaporate water in the vaporizer and  $\dot{W}_{pump}$  is the work required to pump the system water inlet vapor. Exergy of any flow is the maximum theoretical work that can be achieved from that flow in the condition that that flow is only with the heat exchange medium and is brought to the pressure and temperature of the environment, excluding kinetic energies and flow potential, physical to chemical exergy have been obtained from Ref. [11].

Physical Exergy:

$$\dot{E}x^{ph} = (h - h_0) - T_0 (s - s_0) \quad (21)$$

Chemical exergy:

$$\dot{E}x^{ch} = \dot{m} \left[ \sum x_i (ex_i^{ch} - RT_0 \ln x_i) \right] \quad (22)$$

$T_0$  is related to environmental conditions. Also,  $x_i$  is the molar fraction of the material in question in the composition and  $ex_i^{ch}$  is the standard chemical exergy of each component. Specific standard chemical exergy values are determined from reference [40]. The total exergy rate will be as follows:

$$\dot{E}x_{tot} = \dot{E}x^{ph} + \dot{E}x^{ch} \quad (23)$$

By applying the exergy balance to each component of the system, the rate of exergy destruction of that component is obtained:

$$\dot{E}x_D = \dot{E}x_F - \dot{E}x_P \quad (24)$$

$\dot{E}x_P$ ,  $\dot{E}x_F$ , and  $\dot{E}x_D$  refer to the exergy rate of fuel, product, and destruction of each component of the system, respectively. The exergy efficiency of each component can be defined as the ratio of product exergy to fuel exergy [11]:

**Table 1: Validation of the effects of the effect of reactor output temperature on the conversion percentage of methane and carbon dioxide and the amount of hydrogen production per mole of methane a) present model b) Reference [15].**

Temp, °C	600			625			650			675		
	a	b	Var.	a	b	Var.	a	b	Var.	a	b	Var.
%CH <sub>4</sub>	74.77	73.2	2.33	83.84	82.3	1.73	91.7	91.1	0.64	94.6	94.4	0.21
%CO	-15.45	-15.77	1.66	-10.65	-11.23	5.66	-5.48	-5.44	1.08	-0.85	-0.92	5.82
yH <sub>2</sub>	2.38	2.35	1.67	2.61	2.65	0.76	2.75	2.76	1.07	2.88	2.85	0.34

$$\eta_{\text{exe},i} = \frac{\dot{E}x_{\text{product}}}{\dot{E}x_{\text{fuel}}} \quad (25)$$

$\dot{E}x_{\text{Fuel}}$  is also the exergy due to heat transfer in the reactor and evaporator [39]:

$$\dot{E}x_{\text{W,Reactor}} = Q_{\text{Reactor}} \left( 1 - \frac{T_0}{T_{\text{solarsource}}} \right) \quad (26)$$

$$\dot{E}x_{\text{W,vap}} = Q_{\text{vap}} \left( 1 - \frac{T_0}{T} \right) \quad (27)$$

In the above relations,  $T_{\text{solarsource}}$  and  $T$  are the temperatures of the solar source in the reactor and the temperature of the external source in the evaporator, respectively. Also, the input exergy of the biogas-water mixture is obtained from the following equations [1,3].

$$\dot{E}x_{\text{biogas}} = m_{\text{biogas}} \dot{E}x_{\text{tot}} \quad (28)$$

$$\dot{E}x_{\text{water}} = m_{\text{water}} \dot{E}x_{\text{tot}} \quad (29)$$

Thus the exergy efficiency of the whole system is obtained from Equation (30):

Exergy efficiency of the system [39]:

$$\eta_{\text{exe,sys}} = \frac{\dot{E}x_{\text{H}_2}}{\dot{E}x_{\text{biogas}} + \dot{E}x_{\text{water}} + \dot{E}x_{\text{Q,Reactor}} + \dot{E}x_{\text{Q,vap}} + \dot{W}_P} \quad (30)$$

$\dot{E}x_{\text{H}_2}$ ,  $\dot{E}x_{\text{biogas}}$ ,  $\dot{E}x_{\text{water}}$ ,  $\dot{E}x_{\text{Q,Reactor}}$ , and  $\dot{E}x_{\text{Q,vap}}$  is the total hydrogen exergy at the system outlet (flow 12), the biogas, and water inlet exorcism (flow 1,3), and the input exergy due to heat transfer in the reactor and evaporator, respectively.

## RESULTS AND DISCUSSION

In this section, the results obtained from this modeling at different temperatures are validated for the conversion

percentage of methane and carbon dioxide and the amount of hydrogen production with reference [15] in Table 1. The results show good consistency between the calculated parameters in the present work and the based reference.

The composition of the incoming biogas mixture used to analyze the solar biogas reforming system contains 65% methane and 35% carbon dioxide. Other system input information is summarized in Table 2. The hypotheses considered for system exergy analysis are as follows:

- All components of the system work in stable conditions, and heat loss, kinetic energy, potential, and pressure drop for all components are ignored.

- The pressure ratio in the pump (r) is considered equal to 2.

Chemical exergy changes in preheaters, mixers, and evaporators are ignored.

Using the input values considered in Table 2, the solar biogas reforming the system in water vapor to carbon molarity equals 2, and carbon dioxide to methane equals 0.5. The thermodynamic properties of different parts of the system are summarized in Table 3. Also, in Table 4, the types of compounds and molar fractions of currents in different system parts are determined. Examining and analyzing the exergy of the solar biogas reforming system shown in Fig. 2 shows the performance of each system component (control volume) exergetic efficiency for all components and identifies inefficient factors, and improves system degradation. Shown as a Grossman diagram. Table 2 shows the exergetic efficiencies for all system components at reactor temperature and pressure of 698.5 Kpa, 980K, the molar ratio of water vapor to carbon equal to 2, and the ratio of carbon dioxide to methane equal to 0.5, respectively. According to Table 5, the exergy efficiency of the pump is the highest and the exergy efficiency of the reactor is the lowest due to the lower temperature difference between the inlet and outlet flow and the lower consumption work. Also, in Fig. 2, the Grossman diagram shows the use of input



Table 2: Input information for system analysis.

Parameter	value
Biogas mixture composition [15]	35% CO-65% CH <sub>4</sub>
Biogas water vapor reforming reaction temperature (°C)	800
Reactor reaction pressure (bar) [41]	6.8
Molar ratio of water vapor to carbon (S) [41]	2
Molar ratio of carbon dioxide to methane [16]	0.5
Heat power required for the reactor (kW)	1000
Isentropic efficiency of the pump [39]	85%
Molar ratio of water vapor to carbon	2
Minimum temperature difference in advance	20

Table 3: Thermodynamic properties and mass flow calculated for different parts of the solar biogas reforming system.

State	Temperature(C)	Pressure(kPa)	Mass flow(kg/s)	Enthalpy(kW)	Entropy(kJ/K.s)	Ex <sup>ph</sup> (kW)	Ex <sup>ch</sup> (kW)	Ex <sup>tot</sup> (kW)
1	24.5	684.5	0.078	-354.5	-0.1	23.4	4033	4056
2	142.1	684.5	0.078	-332.3	0	27.1	4033	4060
3	24.5	343	0.175	-2298.1	1.7	0	8.8	8.8
4	24.8	684.5	0.175	-2298.1	1.8	0	8.8	8.8
5	122.8	684.5	0.175	-2265.8	1.8	50.7	8.8	56.4
6	161.1	684.5	0.175	-2253	1.8	54.4	8.8	63.1
7	155.3	684.5	0.253	-2585.2	2.7	84.9	4120	4205
8	646.8	684.5	0.253	-2271.6	3.2	261.1	4120	4382
9	696	684.5	0.253	-1291.6	4.2	361.7	4728	5090
10	288.8	684.5	0.253	-1604.3	3.7	176.9	4728	4896
11	161.7	684.5	0.253	-1697.4	3.5	129.5	4728	4858
12	117.1	684.5	0.253	-1729.7	3.5	120.2	4728	4849
13	44.1	684.5	0.253	-1781.6	3.3	111.8	4728	4840

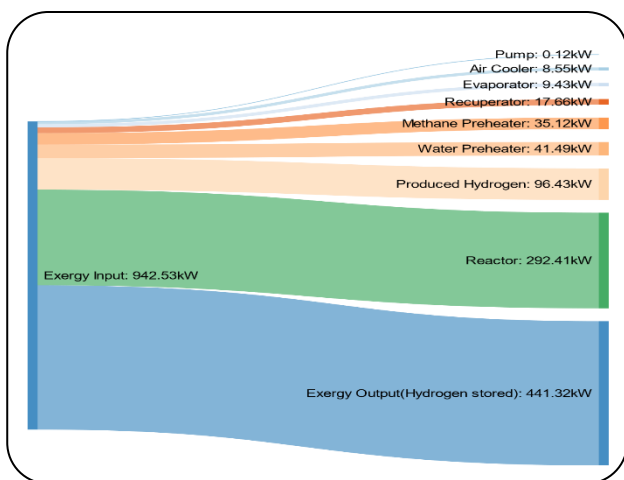


Fig. 2: Exergy Sankey or Grassman diagram of the system.

exergy and its degradation and obtain the hydrogen product's exergy. It is observed that the destroyed exergy in the reactor has the largest share in the destroyed exergy of the whole system.

In the reactor, due to the transfer of heat from the solar source and the chemical reactions of the biogas vapor reforming process, and since the process of heat exchange and chemical reactions is accompanied by entropy production, it, therefore, increases the wasted exergy.

The wasted exergy in the pump also has the lowest share in the wasted exergy of the components due to less labor consumption. According to the diagram, about 10% of the input exergy is related to the exergy of the hydrogen product.

**Table 4: Type of flow combinations in different parts of the system.**

current	Molar Fraction				
	H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	H <sub>2</sub> O
Biogas (1-3)	0	0.65	0	0.35	0
Steam(3-6)	0	0	0	0	1
Reactant(7-8)	0	0.26	0	0.133	0.6
Product(9-13 )	0.51	0.006	0.17	0.082	0.22

**Table 5: The exergy efficiency of each system component.**

Components (control volume)	Exergy efficiency (%)
Methane preheater	94.2
Water preheater	95.2
pump	98.8
Evaporator	85.5
Recuperator	90.4
Reactor	75.5

One factor affecting the solar biogas reforming system is the reaction temperature and the molar ratio of carbon dioxide to methane in the biogas mixture, which affects the amount of hydrogen production, energy efficiency, and exergy of the entire system. 0.5 to 1.5 at different temperatures and shows the molar ratio of water vapor to methane  $S = 2$  at a pressure of 1 bar. By changing this ratio at temperatures below 900 K, not much change is observed in the moles of hydrogen produced, and by increasing this ratio at temperatures above 900 K, the moles of hydrogen produced change, and this change at high temperatures can be explained by Due to the superheated reaction (SMR) and (CMR) and as a result of increasing the reaction temperature, the amount of hydrogen production changes. According to Equation (2) (CMR), more methane at lower molar ratios participates in the reaction with carbon dioxide.

In Fig. 3, at 1035 K, the maximum amount of hydrogen production is 2.9 mol, because at temperatures above this temperature, due to the heating of the WGS reaction equation (3), the equilibrium in the direction of the reactants progresses, and the production rate Hydrogen is reduced. As a result, at different temperatures, the molar ratio of carbon dioxide to methane is 0.5, and the rate of hydrogen production is the highest.

In Figs. 4 and 5, changing the molar ratio of carbon dioxide to methane between 0.5 and 1.5 in the biogas mixture on the energy efficiency and exergy of the whole system for different temperatures and  $S = 2$  at 1 bar reactor pressure is investigated. According to Fig. 1, by increasing the molar ratio of carbon dioxide to methane at temperatures below 900 K, as previously stated (Fig. 3), the amount of hydrogen production is lower, resulting in little change in the energy efficiency of the entire system. But at high temperatures, with increasing this ratio, energy efficiency changes. This change is because with increasing temperature according to Equations (1) and (2), suitable temperature conditions are provided for biogas water vapor reforming reaction, more hydrogen moles are produced, and the system's energy efficiency increases accordingly.

Excessive increase in temperature harms the amount of hydrogen production, and as a result, the energy efficiency of the whole system decreases. Fig. 5 shows a similar process for changing the exergy efficiency of the whole system by changing this ratio.

## CONCLUSIONS

In this study, the energy analysis and exergy of the solar biogas water vapor reforming system for hydrogen production were investigated. Also, different system parameters such as reactor temperature, the molar ratio of water vapor to carbon, and the molar ratio of carbon dioxide to methane in biogas mixture on hydrogen production, energy efficiency, and exergy efficiency of the whole system were evaluated. The important results obtained in this research can be summarized as the exergy wasted in the reactor has the largest share in the wasted exergy of the whole system; the highest amount of hydrogen production in this system under conditions, when  $S = 2$  and the molar ratio of carbon dioxide to methane is 0.5, temperature 1035K and pressure 1 bar, was 2.9 mol per mole methane; for the best system condition,

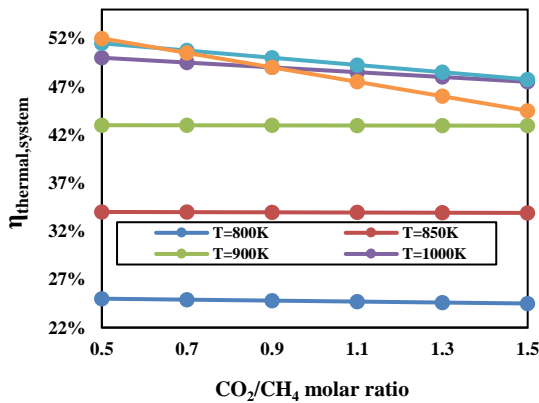


Fig. 3: Effect of molar ratio of carbon dioxide to methane on hydrogen production per mole of methane at different temperatures and 1 bar pressure

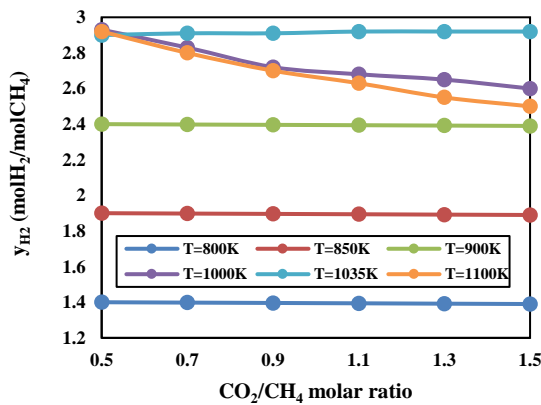


Fig. 4: Effect of molar ratio of carbon dioxide to methane on energy efficiency the whole system at different temperatures and SC= 2 and pressure 1 bar e.

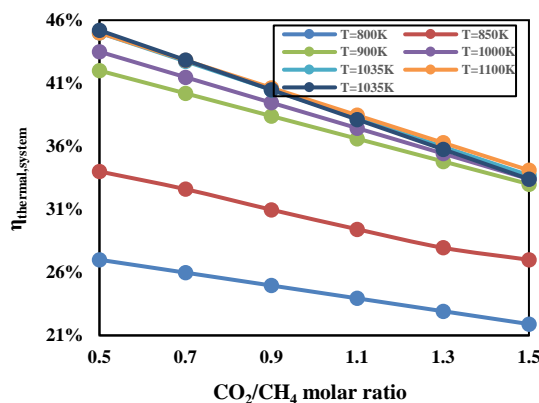


Fig. 5: Effect of molar ratio of carbon dioxide to methane on the exergy efficiency of the whole system at different temperatures and SC= 2 and pressure 1 bar.

the highest energy efficiency and exergy of the whole system are 52% and 42%, respectively; by increasing the reaction temperature at a constant molar ratio of water vapor to carbon and the constant molar ratio of carbon dioxide to methane in the biogas mixture at atmospheric pressure, first, the amount of hydrogen production reaches its maximum, and too much temperature harms hydrogen production, also, by increasing the molar ratio of water vapor to carbon at a certain temperature, hydrogen production increases. A similar trend is achieved by changing the temperature and molar ratio of water vapor to carbon on the energy efficiency and exergy of the whole system; and By increasing the molar ratio of carbon dioxide to methane in the biogas mixture at low temperatures, with little change in hydrogen production, energy efficiency, and exergy has not been achieved. At high temperatures, changing this ratio reduces hydrogen production per mole of methane and consequently opens energy, and the exergy of the whole system is reduced.

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